Neutron Scattering Studies of Hybrid Perovskites for Photovoltaic Applications

M.K. Crawford
DuPont CR&D

40 Years of Neutron Scattering Symposium
NIST Center for Neutron Research
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  - For DCS
  - For your help to members of the PAC Committee
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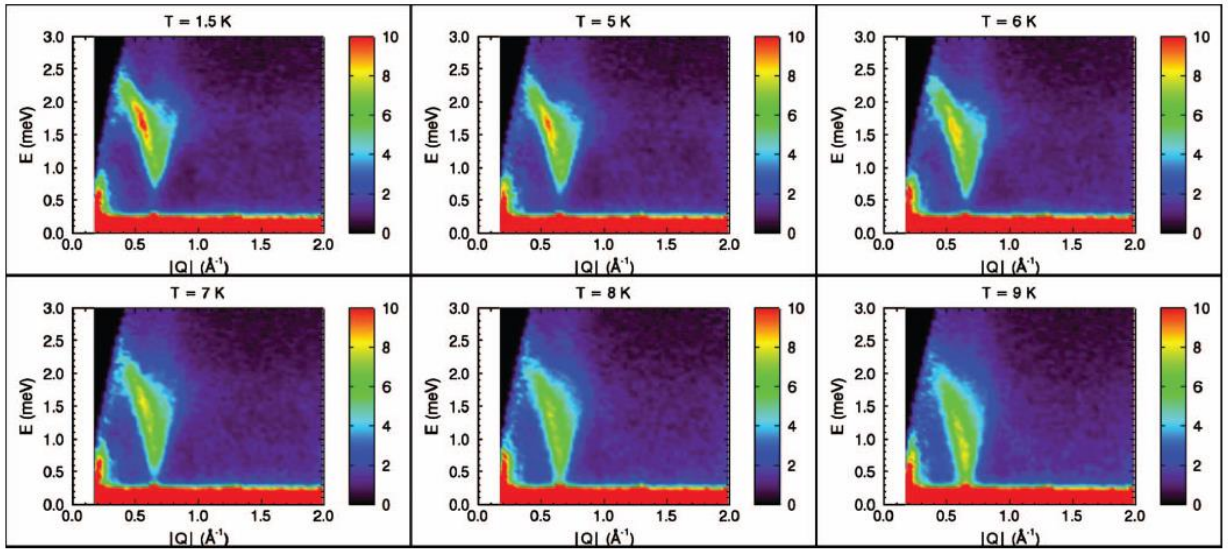
- You have both contributed greatly to the science and culture of the NCNR
  - And I hope you continue to do so in retirement

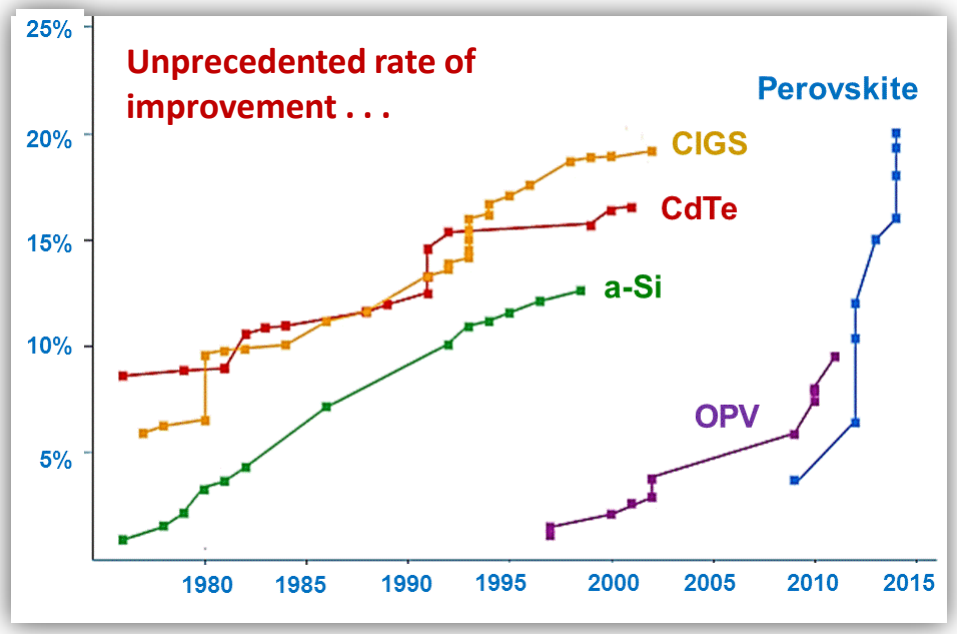
My One DCS Experiment: Spin Waves in $GeNi_2O_4$

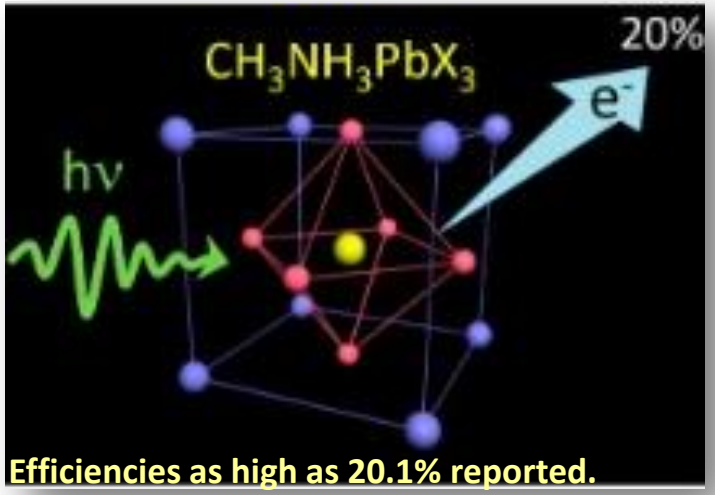


Lashley et al, Phys. Rev. B **78**, 104406 (2008)

- $GeNi_2O_4$
  - Antiferromagnetic cubic spinel
  - Two Neel transitions: 12.1 K and 11.4 K
- DCS S(Q,ω) beautifully shows
  - 0.3 meV spin wave gap
  - Nicely dispersing spin waves

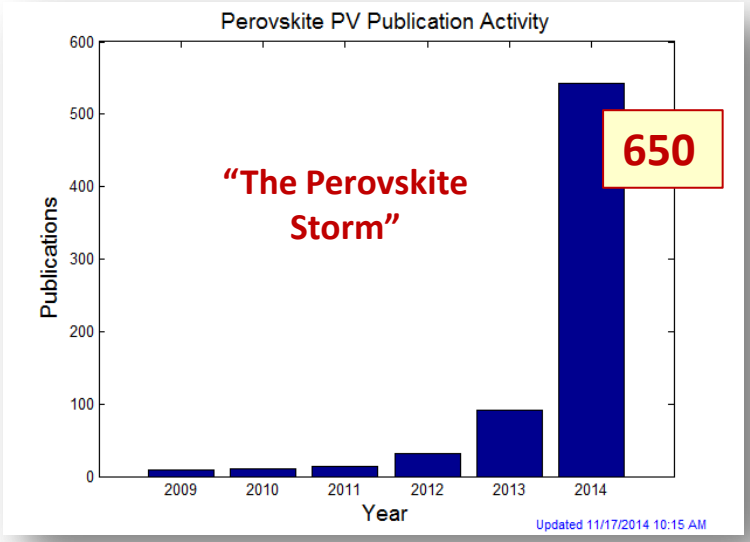
The Rise of Hybrid Perovskites for Photovoltaics





Exceptional Properties

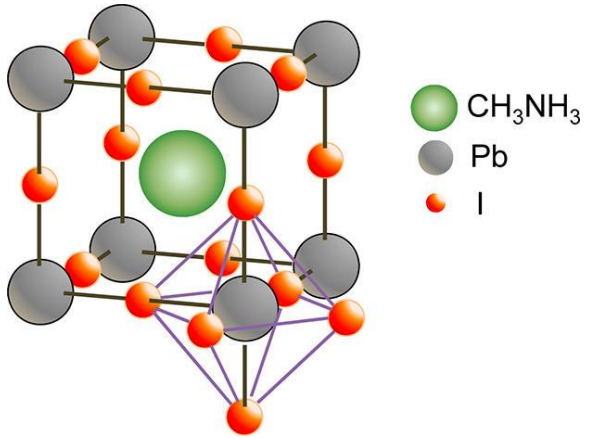
- **Ambipolar conductivity**: p- or n-type semiconductor
- **Carrier diffusion lengths : > 1 μm**
- **High defect tolerance**
- **Ideal bandgap** of 1.55 eV for $MAPbI_3$ (tunable)
- **High Voc** (>1 V)
- **Low Voc Deficit** (69% of bandgap)



Perovskites

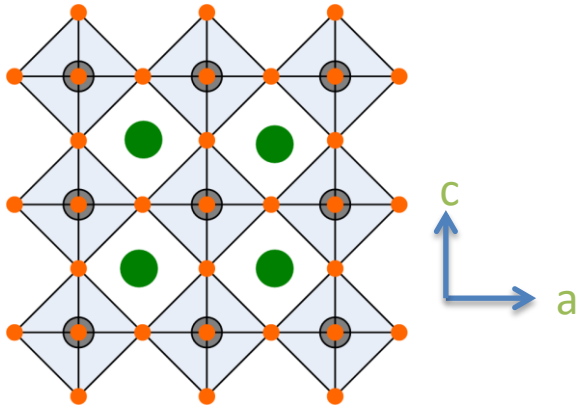
ABX_3

- Hundreds of perovskites: Properties vary and include insulating, antiferromagnetic, piezoelectric, thermoelectric, semiconducting, conducting, and superconducting materials
- $(MeNH_3)PbI_3$ ($MAPbI_3$): "Standard" composition for perovskite-based PV, including record devices, with bandgap of 1.6 eV



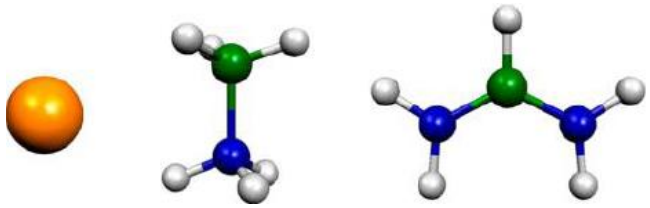
Structure

- 3D network of corner sharing PbI_6^{3-} octahedra with charge-compensating cations in the gaps



Bandgap of $MAPbI_3$ is readily tuned by chemical substitution:

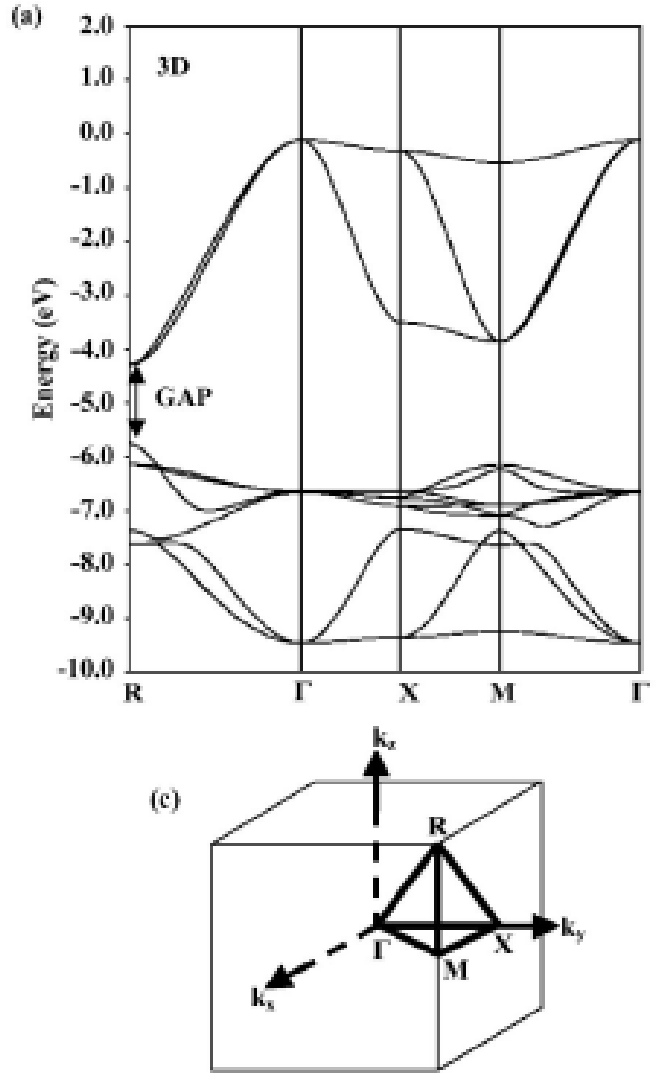
- Halide substitution, e.g. $MAPb(Br_xI_{1-x})_3$: 1.6 to 2.2 eV
- Metal substitution, e.g., $MASnI_3$: 1.3 eV
  - *Sn oxidation to Sn(IV) leads to degradation*
- Cation substitution: Cs, 1.7 eV; FA, 1.5 eV
  - *$CsPbI_3$ readily decomposes*
  - *Cation must be small enough to fit within the gap (tolerance factor)*



Cs^+ **$CH_3NH_3^+$** **$HC(NH_2)_2^+$**

MA FA

$MAPbI_3$ Brillouin Zone and Band Structure



- Cubic perovskite Pm-3m
- Direct bandgap semiconductor
  - High optical absorption coefficient
  - Thin films harvest light effectively
- High symmetry Brillouin zone boundary points
  - R, M, X
  - Optical bandgap is located at the R point
  - R point becomes the Γ point in the tetragonal phase
- T. Umebayashi et al, PRB 67, 155405 (2003)

Hybrid perovskite crystal structures are complex

- Presence of organic cations generates large amounts of disorder at high temperatures where PV devices operate
- Structural phase transitions involving rotations of PbI_6 octahedra, coupled to organic cation reorientations through hydrogen bonds, have significant impact on physical properties such as
  - Charge carrier mobility
  - Ionic conductivity
  - Exciton binding energies
  - Optical absorption
  - Thermal conductivity
  - Heat capacity

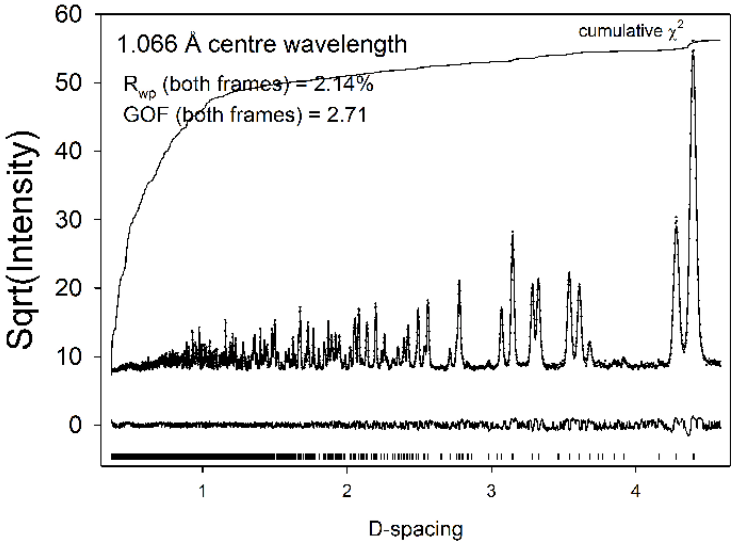
Structures: Neutron and X-Ray Diffraction

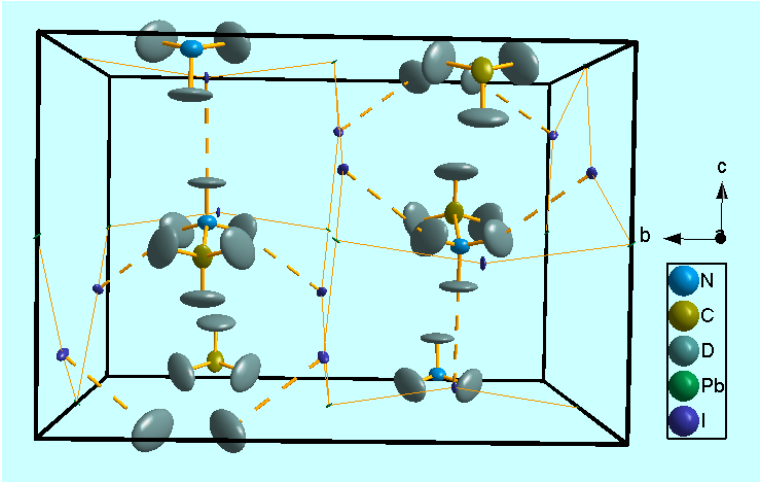
- Neutron diffraction data collected at POWGEN/SNS
- Fully and partially deuterated samples
  - Reduce incoherent scattering
  - Measure isotope effects on phase transitions
  - C, N and H/D atom positions

- X-ray diffraction data collected at Advanced Photon Source
  - DND-CAT
  - 0.4 Å wavelength (31 keV)
  - High resolution

Element	Neutron Coherent Cross-section (barn)	X-Ray Cross-section (barn)
H	1.76	0.6
D	5.59	0.6
C	5.56	5
N	11.0	6.5
Pb	11.12	9392
I	3.5	1622

Orthorhombic structure: T = 10 K

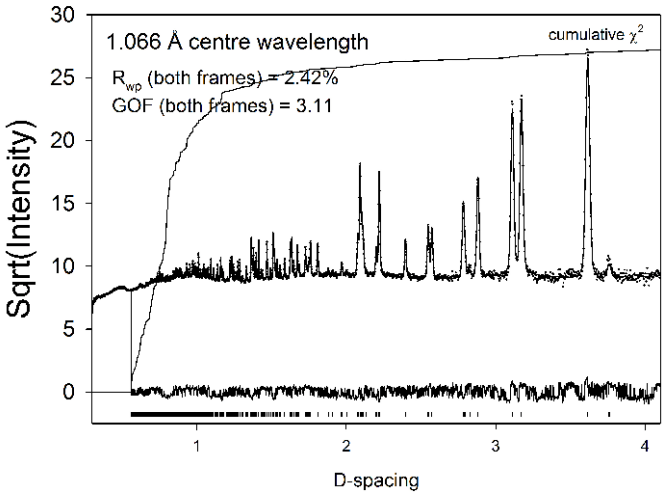


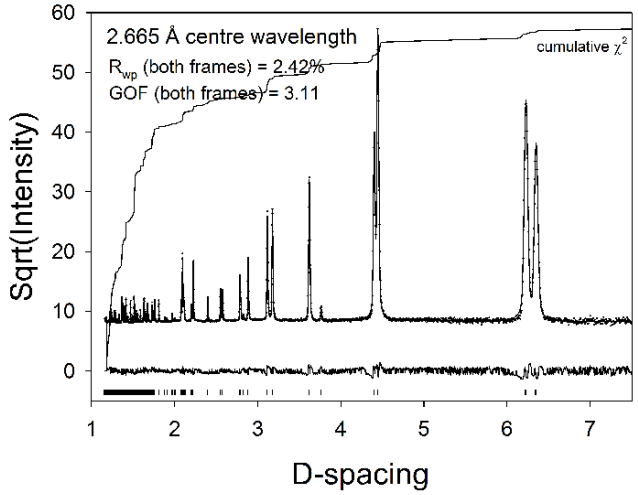


95% ellipsoids

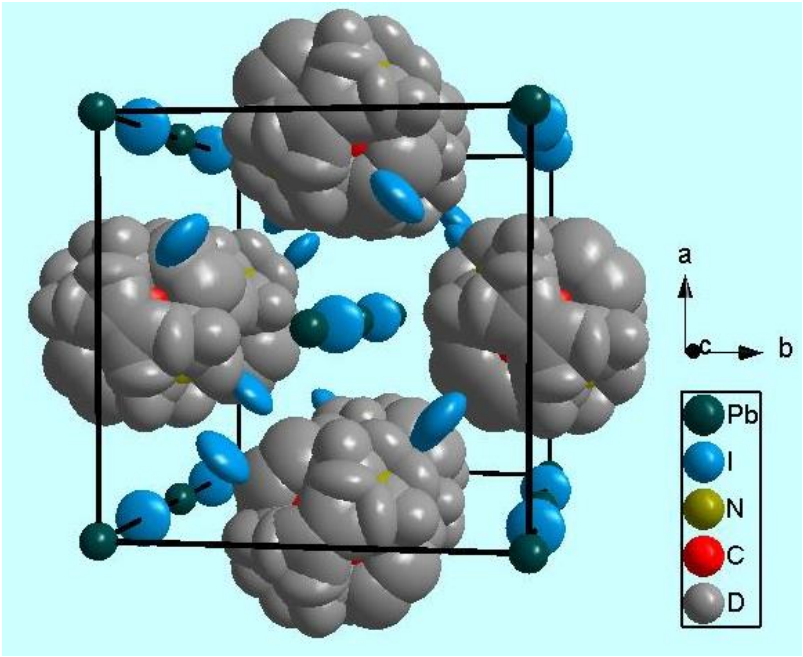
- Pnma structure refinement
  - T = 10 K to minimize diffuse background contribution
  - Scattering to high Q – some diffuse background even at 10K
  - Full un-constrained refinement carried out.
  - Same structure as $MAPbBr_3$ at 10 K (Swainson et al.)
- Three strong hydrogen bonds between D and the I(2) sites of 1 x 2.625 Å/179.5º and 2 x 2.696 Å/150.6º
- Deuterium ADPs as expected for such a structure
- Pb and I ADPs small with little directional motion by the iodines

Tetragonal structure: T = 190K



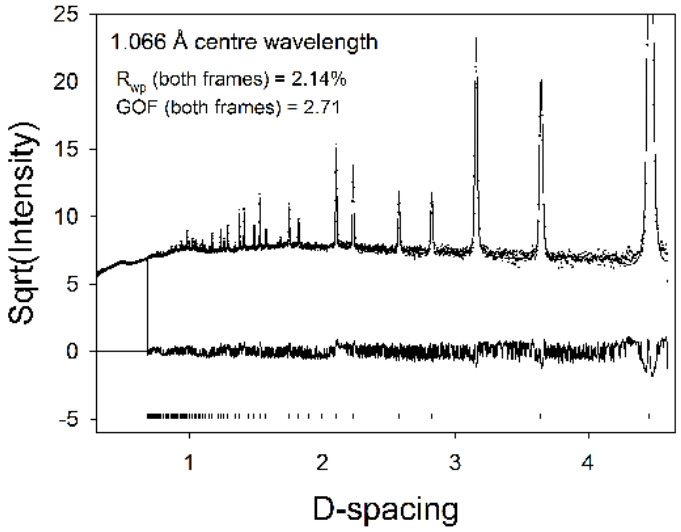


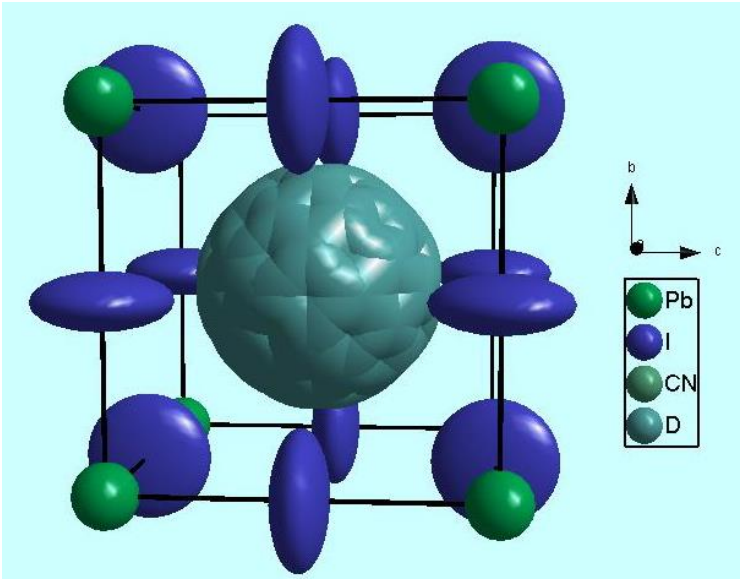
- I4/mcm symmetry
  - Same as Weller structure: Chem Commun (2015)
  - C and N ¼ occupancy, D $^1/_8$ occupancy; 8 positions
- D-I distances on order of 3.0 Å: weaker H-bonds



95% ellipsoids

Cubic structure: T = 350K

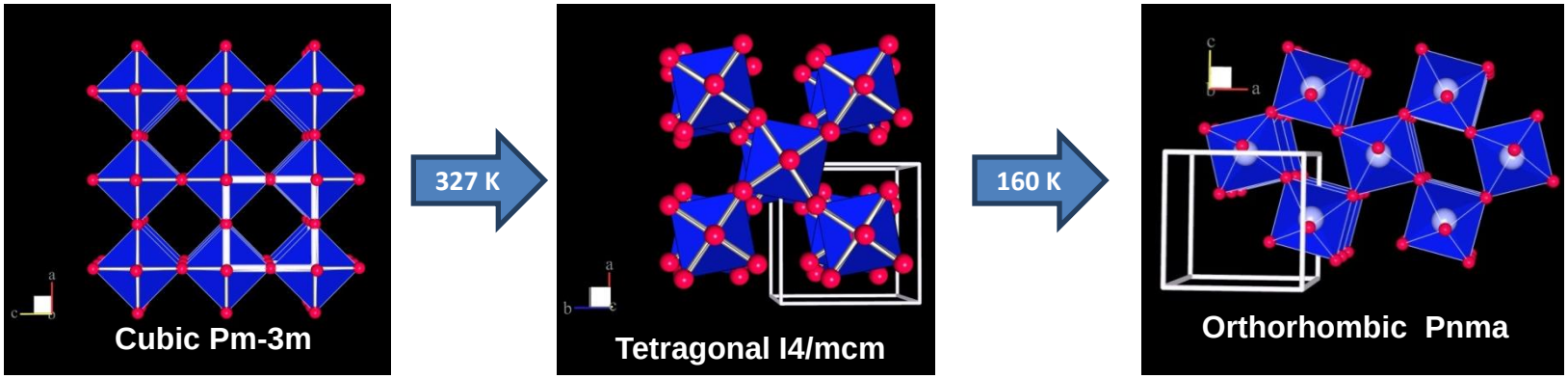




95% ellipsoids

- Pm-3m symmetry
- Despite extreme disorder
  - Only 5 atomic positions so no constraints needed
  - Very significant diffuse background which was partially modelled using a sin(q)/q curve to reduce number of background parameters
  - Structure agrees with literature structure
- MA is completely disordered as a nearly free rotor.
- Iodine ADPs similar size to the deuterium atoms
- Closest centroid D-I distance 3.09 Å
  - Weak hydrogen bonds

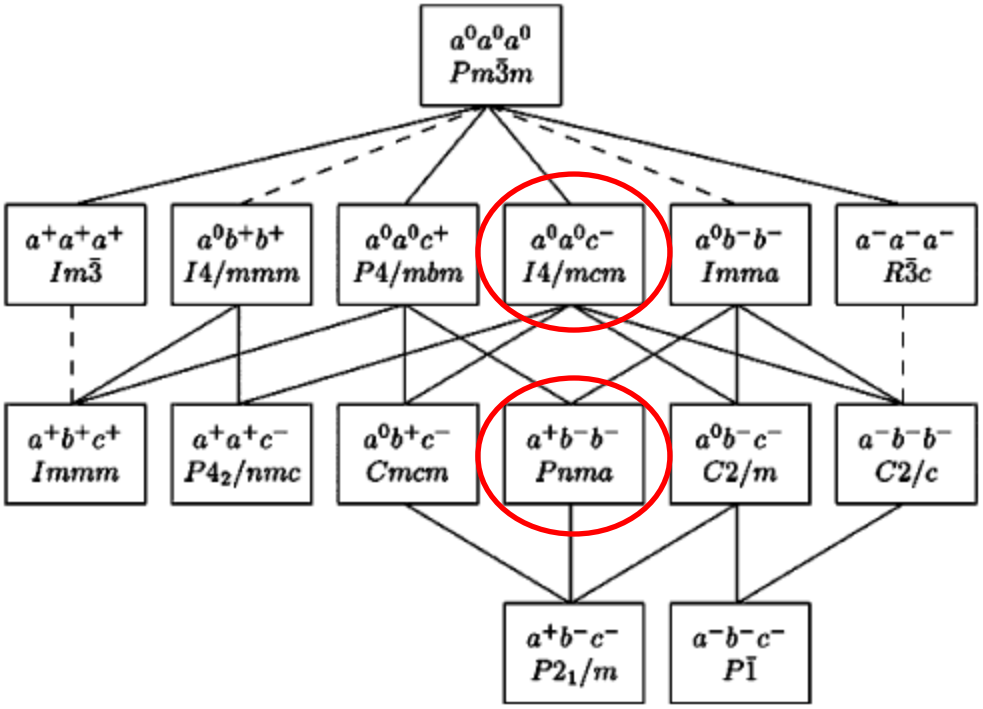
$MAPbI_3$ Structures

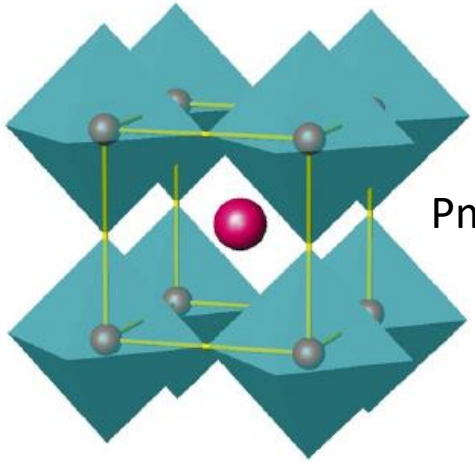


- Only showing the PbI_6 octahedra
- Cubic-tetragonal transition involves rotations of octahedra around a single cubic axis
  - Order parameter is rotation angle
- Tetragonal-orthorhombic transition involves tilts around additional cubic axes

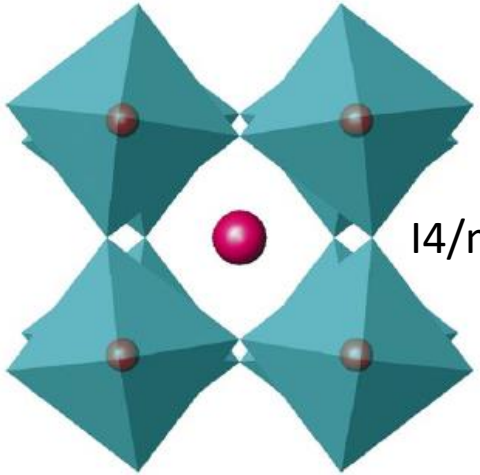
Structural phase transitions in $MAPbI_3$

Space Group	Glazer Notation for Octahedra Tilts and Rotations
Pm3m	$a^0a^0a^0$
I4/mcm	$a^0a^0c^-$
Pnma	$a^+b^-b^-$





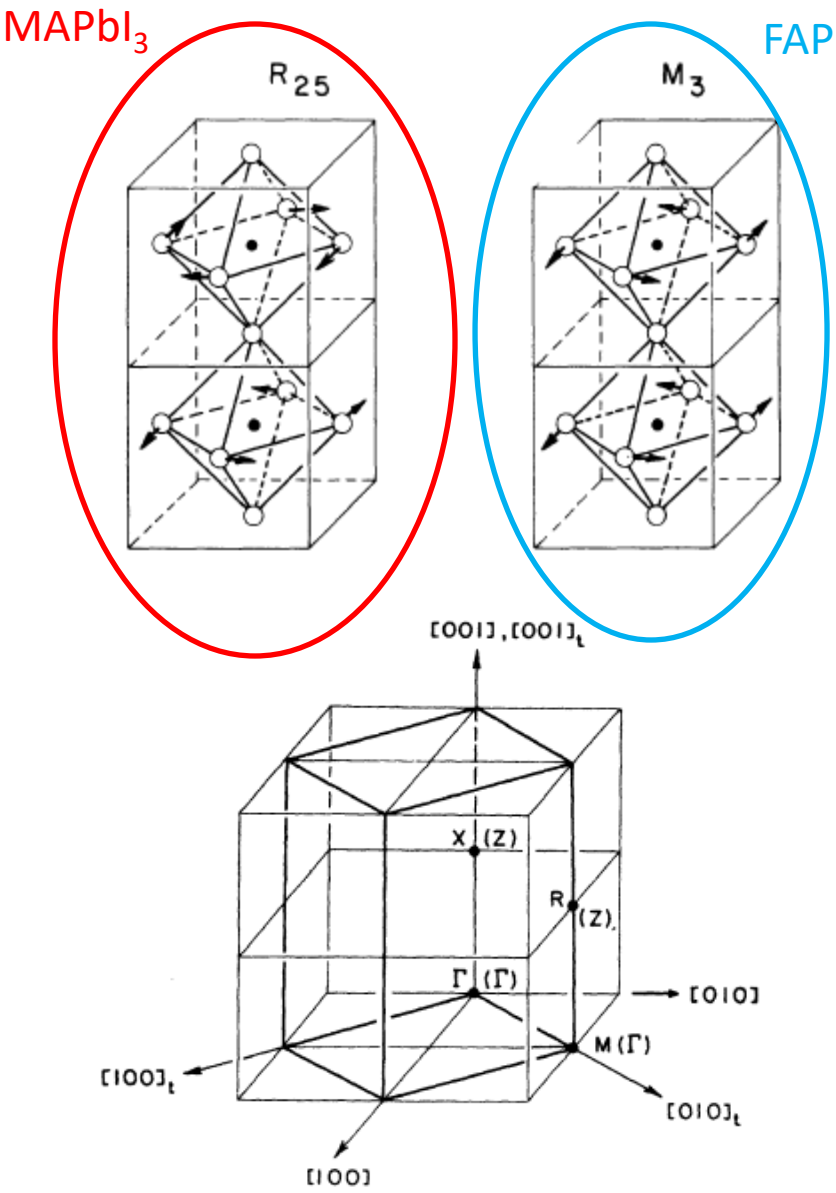
Pm3m



I4/mcm

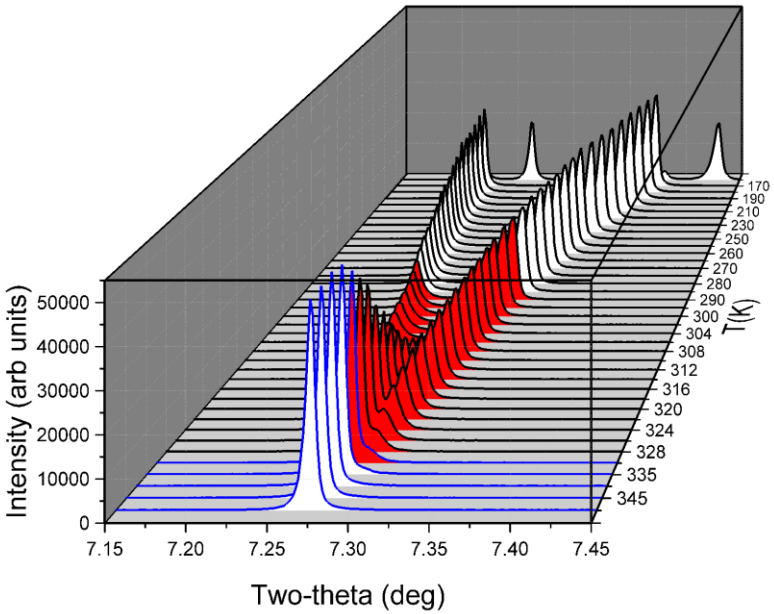
Howard and Stokes, Acta Cryst B54, 782 (1998)

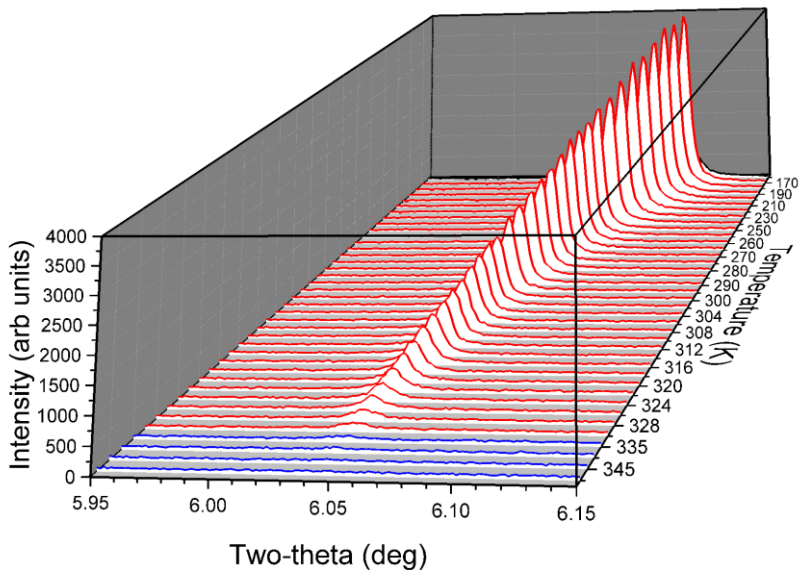
Hybrid Perovskite Phase Transitions



- Cubic-tetragonal phase transition of $MAPbI_3$
  - Similar to cubic-tetragonal transition in $SrTiO_3$ at 110 K
  - Driven by condensation of single triply degenerate R-point phonon (out-of-phase rotation around cubic c axis)
  - Superlattice Bragg peaks appear with cubic indices ½ (hkl) with h, k, l odd
  - I4/mcm
- Low temperature transition involves cubic M and X-point phonons
  - Rotations around different cubic axes
  - But coupled to order-disorder transition of MA cations through hydrogen bonds

X-Ray Bragg Reflections and PbI_6 Rotations: d6-$MAPbI_3$



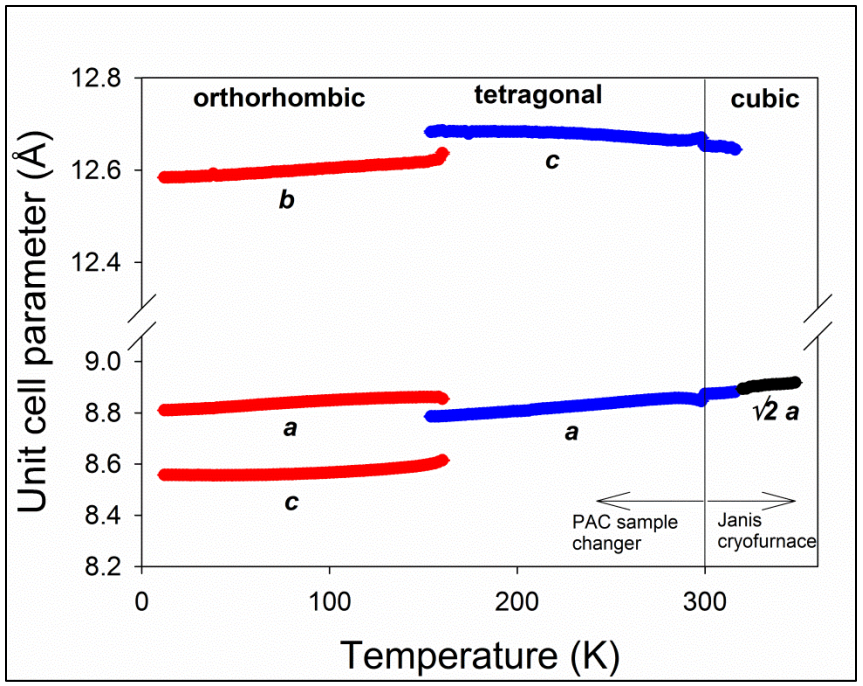


- Cubic-tetragonal phase transition at T = 330 K
  - First-order (phase coexistence)
- (200) cubic Bragg reflection
  - Splits into (220) and (004) tetragonal Bragg peaks
  - Tetragonal strain is a secondary order parameter

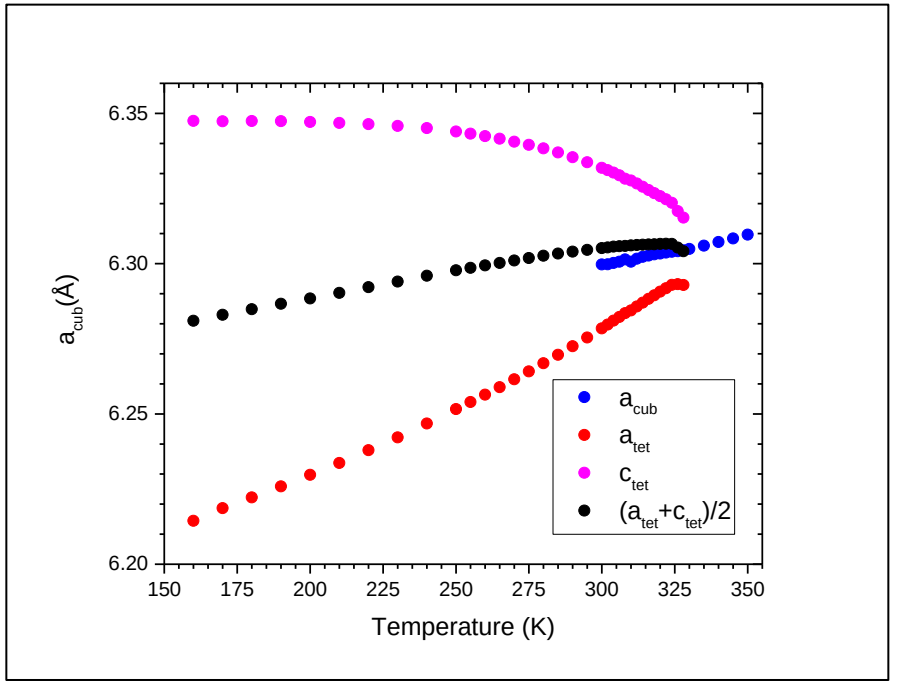
- R-point ½ (311) Bragg reflection
  - Pseudo-cubic unit cell
  - Same as (211) in tetragonal cell
  - **Shows the presence of out-of-phase PbI_6 rotations**
  - **I4/mcm space group**

$MAPbI_3$ Lattice Parameters: Neutron and X-Ray Diffraction

Neutron

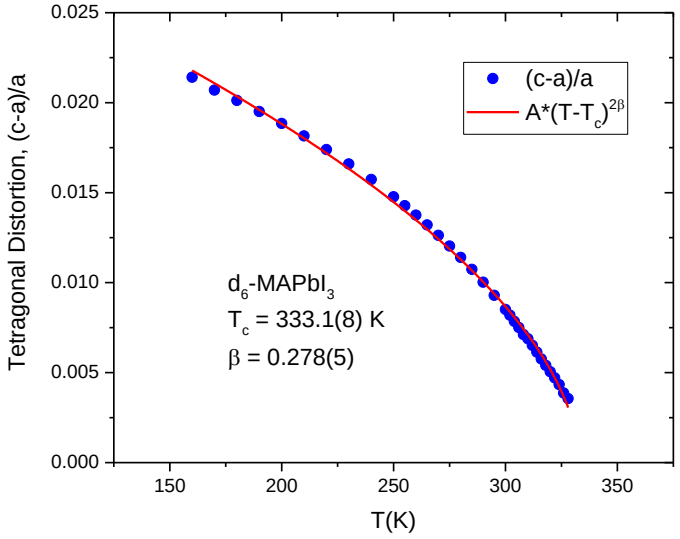


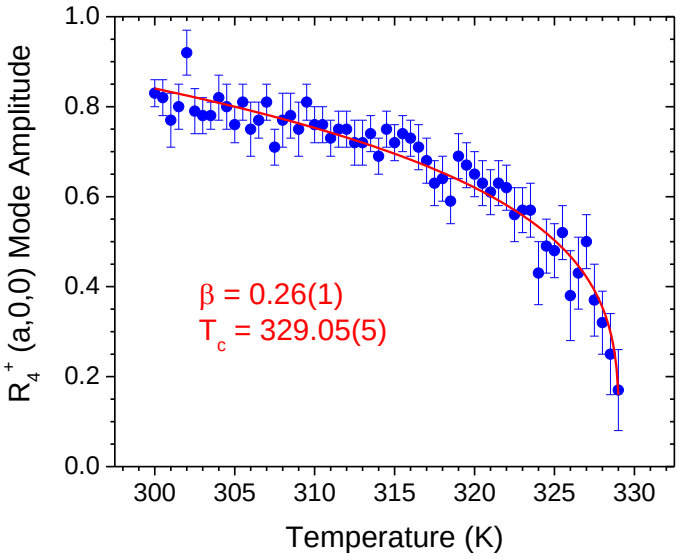
X-Ray



- Two structural phase transitions
  - High temperature transition nearly continuous , but XRD shows phase coexistence
  - Lattice parameters show discontinuities at low temperature structural transition at 160 K

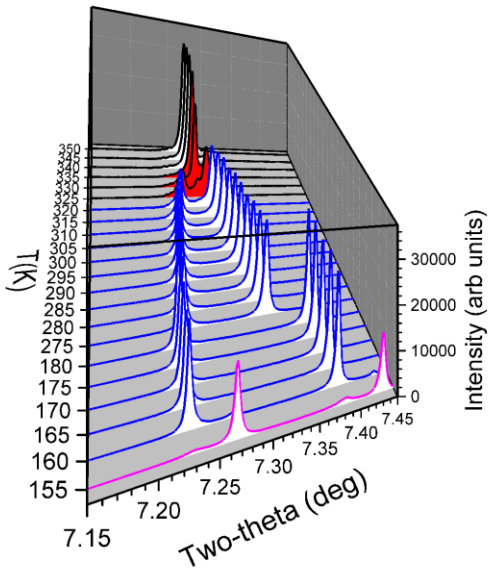
Order Parameter for Cubic-Tetragonal Phase Transition: d6-$MAPbI_3$

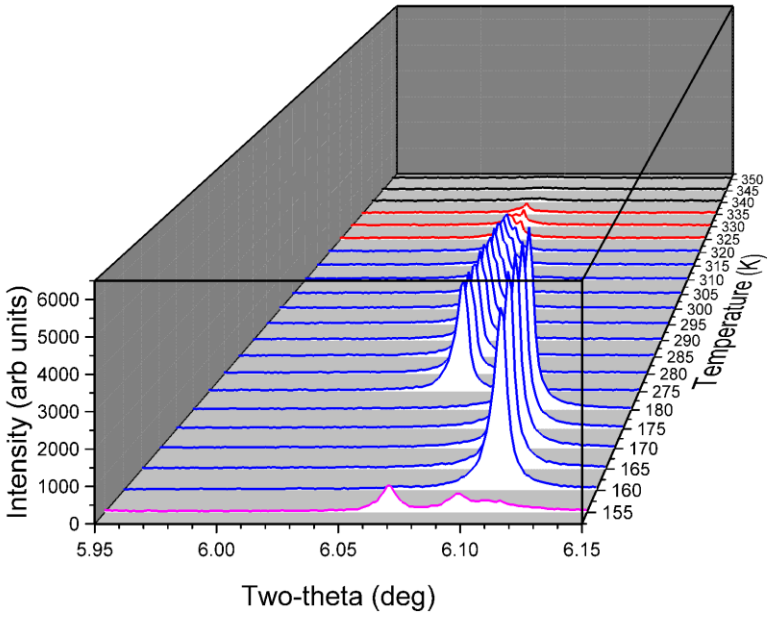




- X-ray and neutron diffraction both show phase transition is close to tricritical (intersection of first and second order transitions)
  - Tetragonal distortion from x-ray diffraction
  - Distortion mode analysis from neutron diffraction
  - Order parameter scales with $(T_c\text{-}T)^{0.25}$

Bragg Reflections and PbI_6 Rotations: h6-$MAPbI_3$

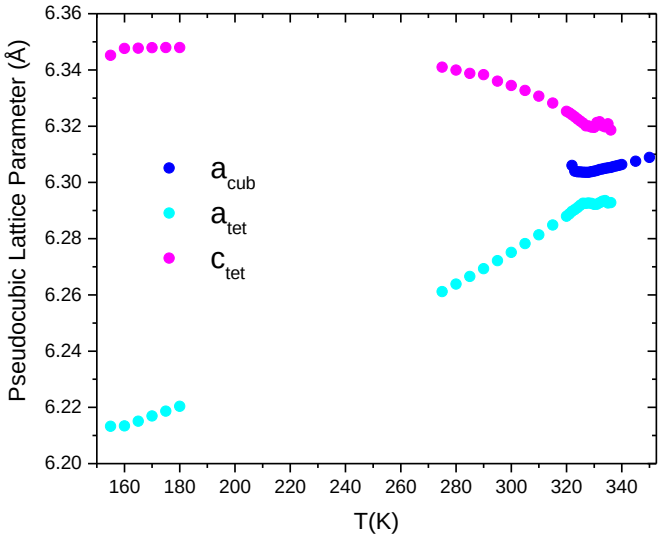


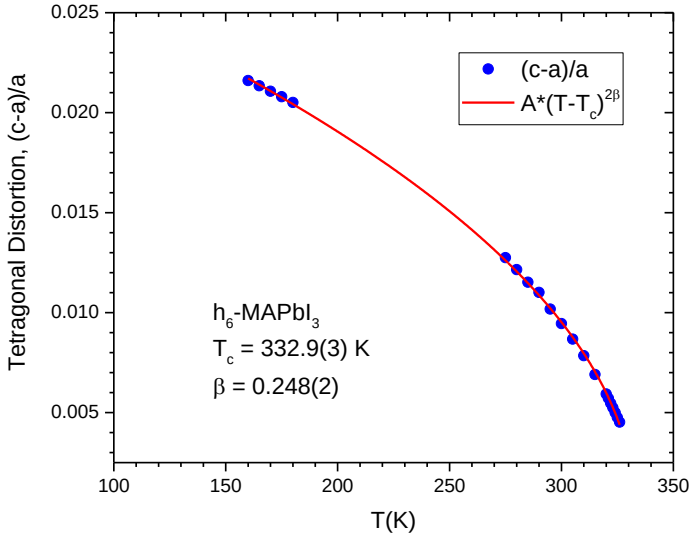


- Cubic 200 Bragg peak
  - Splits into (220) and (004) Bragg peaks in tetragonal phase
  - Phase coexistence
    - Narrower region than d6-$MAPbI_3$

- Tetragonal (211) superlattice Bragg peak
  - ½ (311) in cubic cell
  - Pnma phase appears via first-order transition at T = 160 K

Order Parameter for Cubic-Tetragonal Phase Transition: h6-$MAPbI_3$

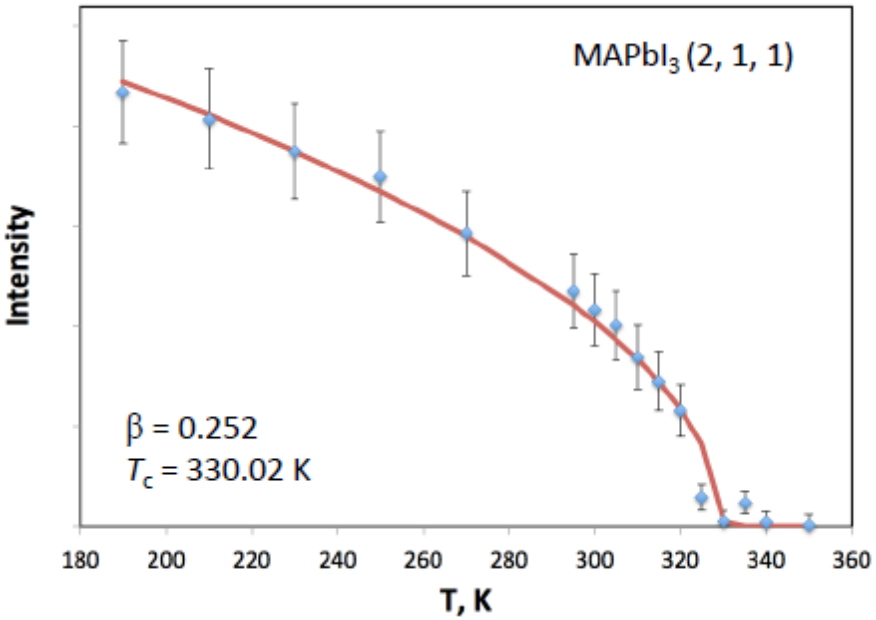




- Tetragonal distortion vs T
- Small region of cub0c-tetragonal coexistence

- Tetragonal distortion vs T
  - $(T_c - T)^{2\beta}$
  - $\beta = 0.248$
  - Tricritical

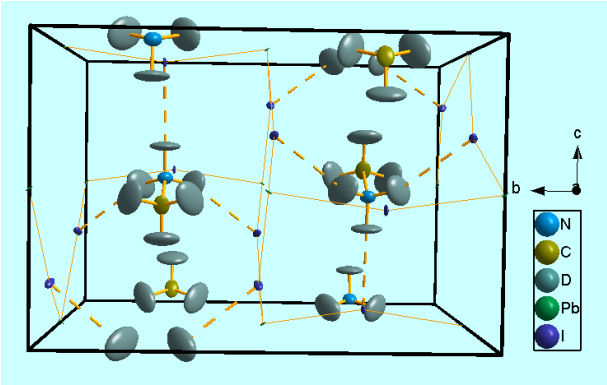
d6-$MAPbI_3$ Single Crystal Diffraction on TOPAZ at SNS



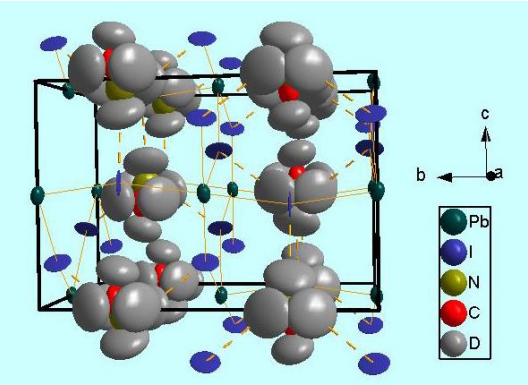
- d6-$MAPbI_3$ single crystal
  - 1-2 mm in size
- Tetragonal (211) Bragg reflection
  - Superlattice ½ (311) in pseudocubic cell
  - Power law fit again consistent with near-tricritical behavior

$MAPbI_3$ phase transitions: MA disorder grows with temperature

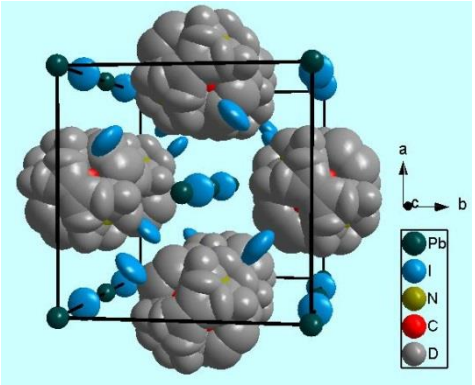
Pnma T = 10 K



Pnma T = 130 K



I4/mcm T = 190 K

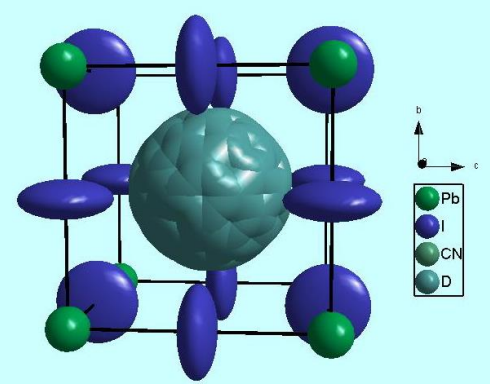


Orthorhombic

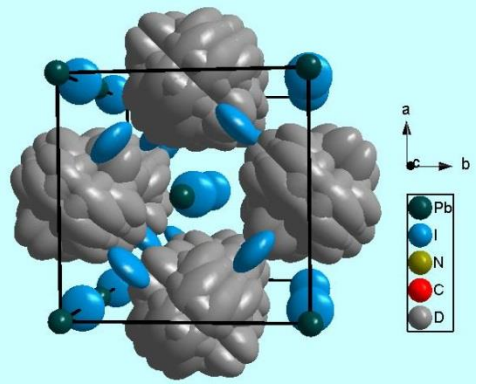
160 K

Tetragonal

Pm-3m T = 350 K



I4/mcm T = 300 K

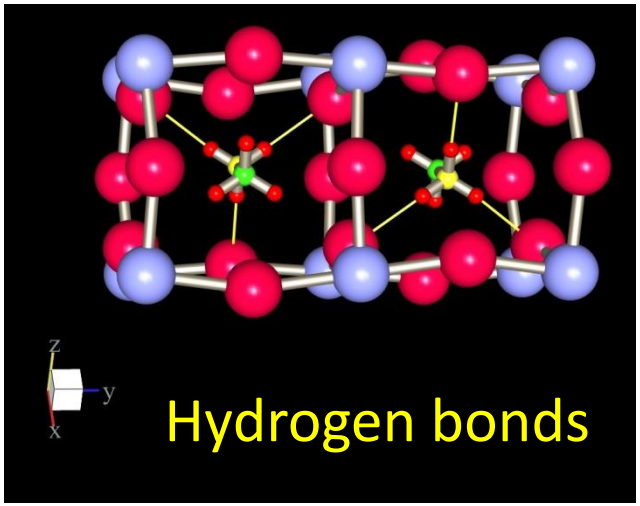


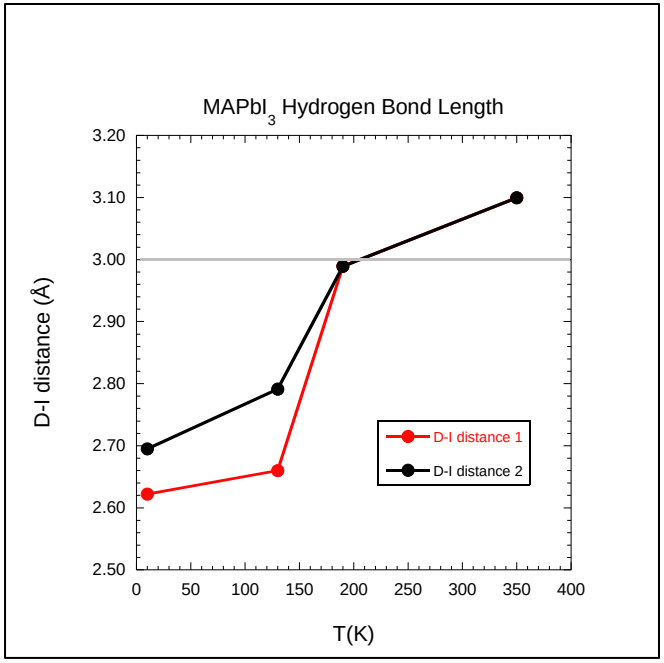
Cubic

330 K

Tetragonal

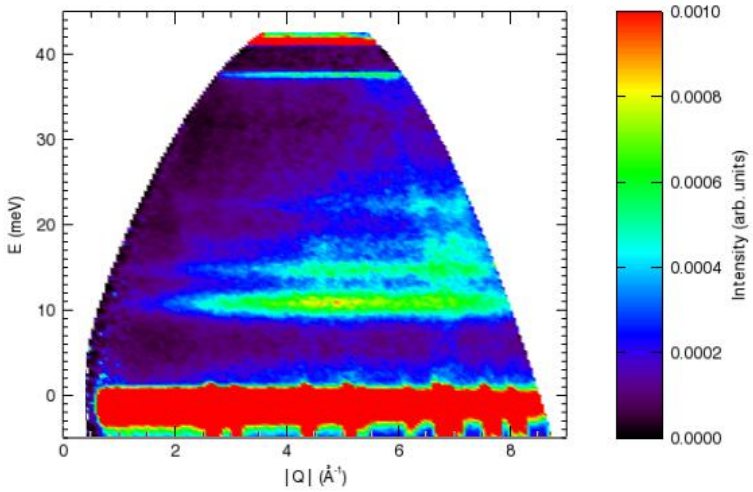
Hydrogen bonds play a role in structural transitions

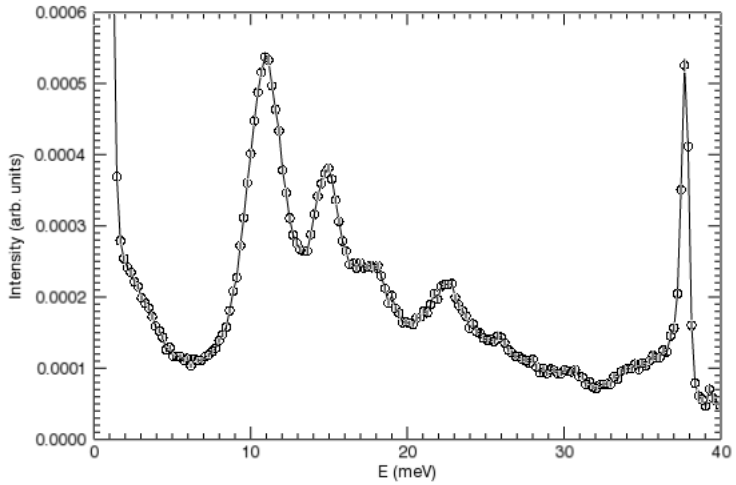




- Hydrogen bond strengths are directly correlated with structural phase transition at 160 K
  - Low temperature orthorhombic structure has strongest H-bonds
  - Order-disorder transition of MA cations
- H-bonds decrease in strength with increasing temperature
  - Thermal expansion
  - MA cation disorder

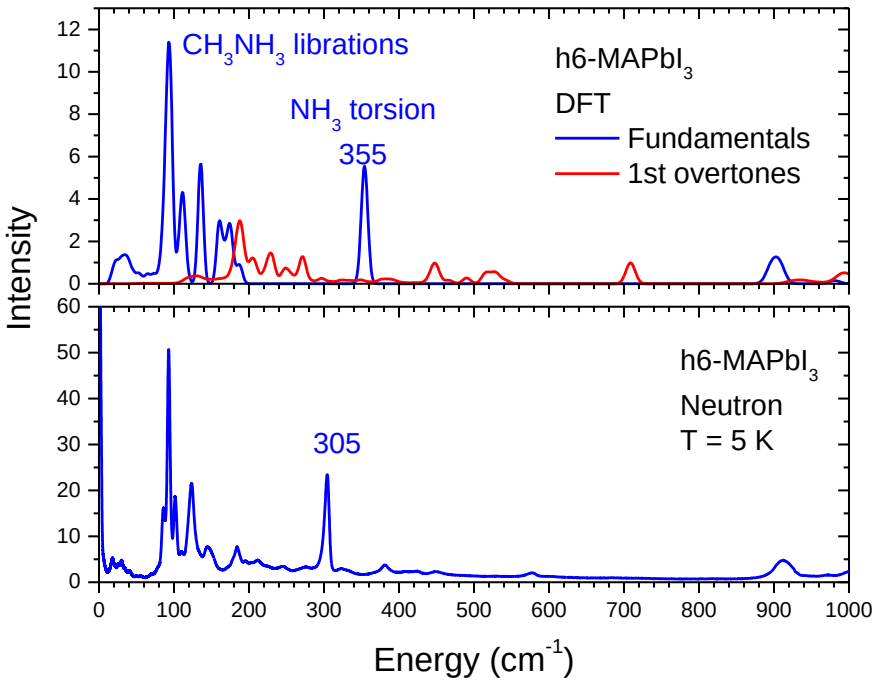
Neutron Spectroscopy of h6-$MAPbI_3$: dispersion





- CNCS spectrometer at SNS
  - T = 1.7 K
- MA vibrations have little dispersion
  - Molecular vibrations
  - Intermolecular coupling is weak
- Peak assignments (from DFT)
  - 10-25 meV peaks correspond to CH_3 torsions, and librations and translations of MA cations
  - Peak at 38 meV is intramolecular vibration, mostly NH_3 torsion

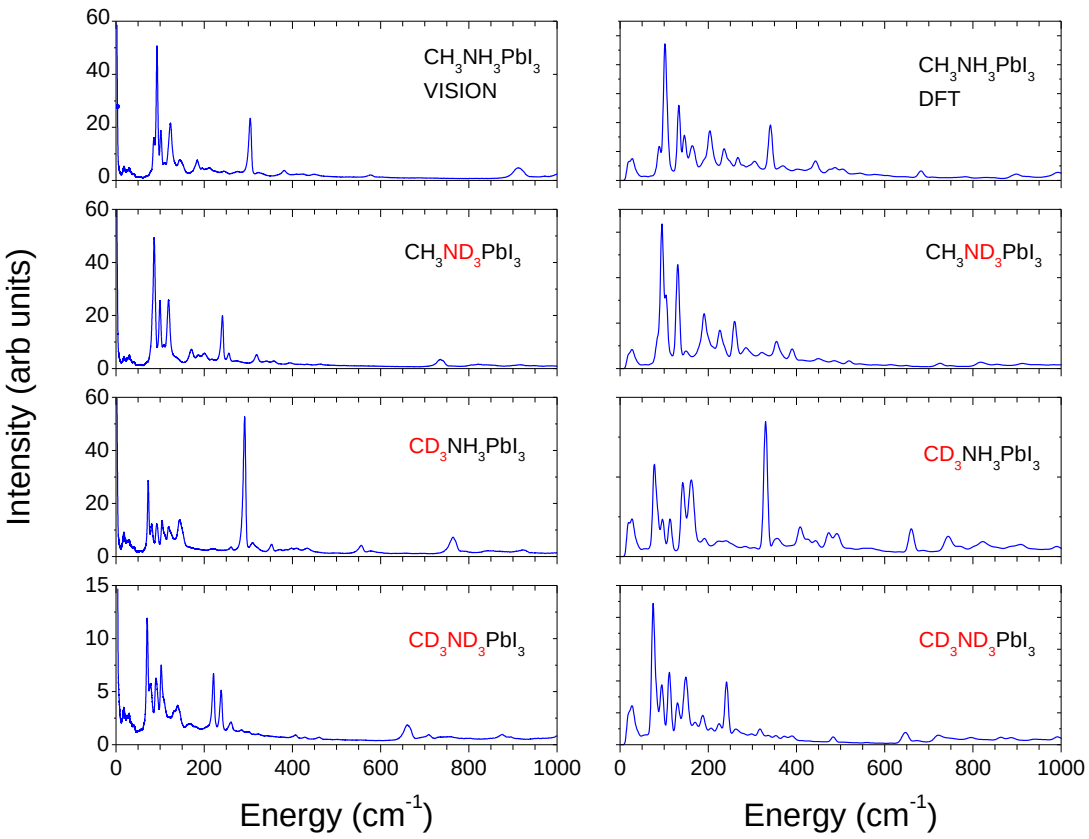
$MAPbI_3$: Neutron Vibrational Spectra and DFT Calculations



Comparison of neutron and DFT spectra provides a demanding test of accuracy of DFT calculation

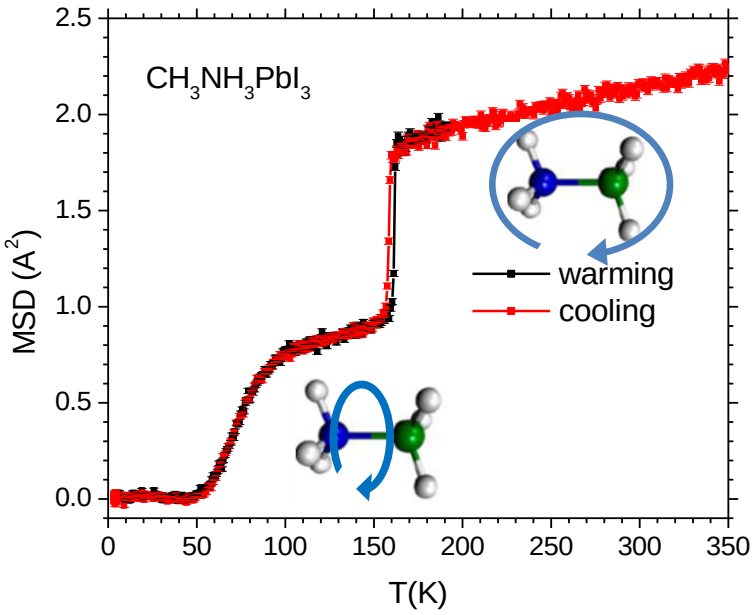
- VISON spectrometer at SNS
  - T = 10 K
- Neutron vibrational spectrum
  - Similar to IR and Raman, but no selection rules
  - MA vibrations dominate due to large incoherent neutron scattering cross-section for H
- Density functional theory
  - Vibrational eigenvectors
    - Use as input to calculate neutron spectrum
  - Provides vibrational mode assignments
    - I. Milas (DuPont) and Y.Q. Cheng (ORNL)
- Measurements of vibrations and phonons are important for understanding
  - Electron-phonon coupling (charge transport)
  - Thermal conductivity (heat capacity)

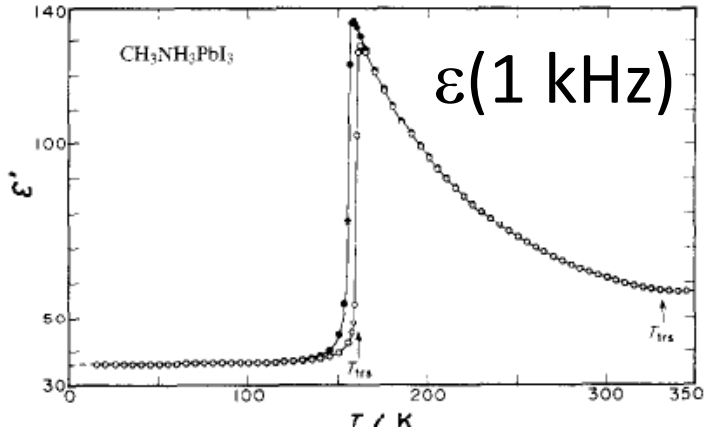
$MAPbI_3$ neutron vibrational spectra vs DFT



- Partially and fully deuterated samples
  - Establish vibrational mode assignments
    - "NH_3 torsion" at 37.7 meV shifts significantly upon deuteration
      - υ_H/υ_D = 1.26 (vs 1.41)
    - "CH_3 torsion" at 11.5 meV shifts to 9 meV upon deuteration
      - υ_H/υ_D = 1.26 (vs 1.41)
  - Test accuracy of vibrational eigenvectors from DFT calculations

QENS: Structural transitions affect dielectric properties





Onoda-Yamamuro et al, J Phys Chem Solids 53, 935 (1992)

Mean square displacement (MSD) measured using HFBS at NIST Center for Neutron Research

- Calculated from elastic peak intensity vs T
- Measure of mobility of methylammonium (MA) cations

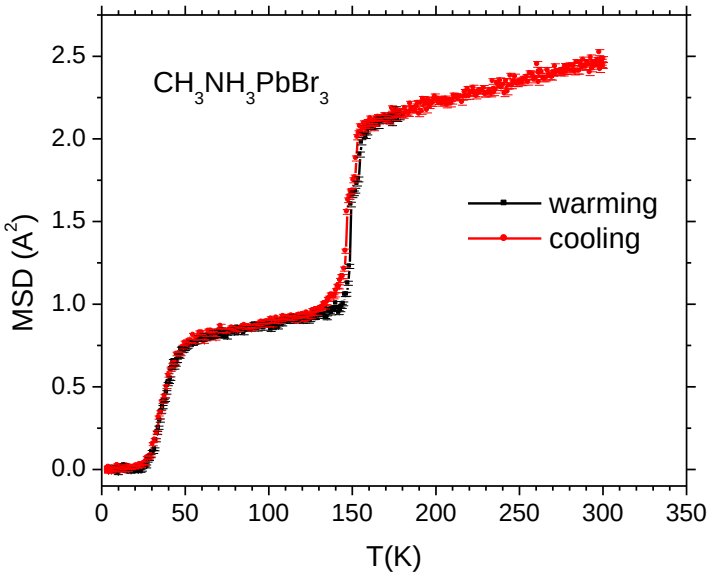
Dielectric constant tracks mobility of the MA cations at structural phase transitions

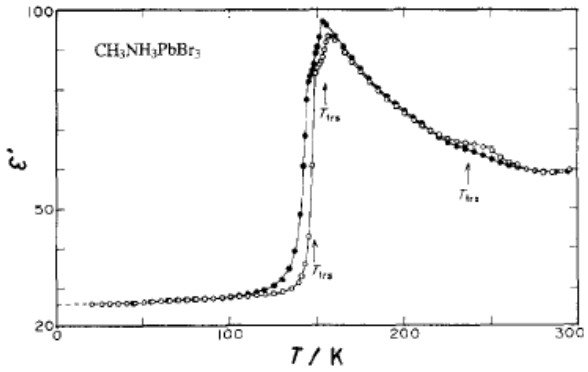
- **T < 160 K** – Low dielectric constant
  - MA cations are fully ordered, dipoles no longer reorient in response to electric field
  - Dynamics due to rotations around C-N bond
- **T > 160 K** – High dielectric constant
  - Nearly free rotation of MA cations above transition leads to large dielectric constant
  - Cubic-tetragonal transition at 330 K does not affect MA cation dynamics or dielectric properties

High dielectric constant in cubic and tetragonal phases reduces exciton binding energy → increases charge separation efficiency

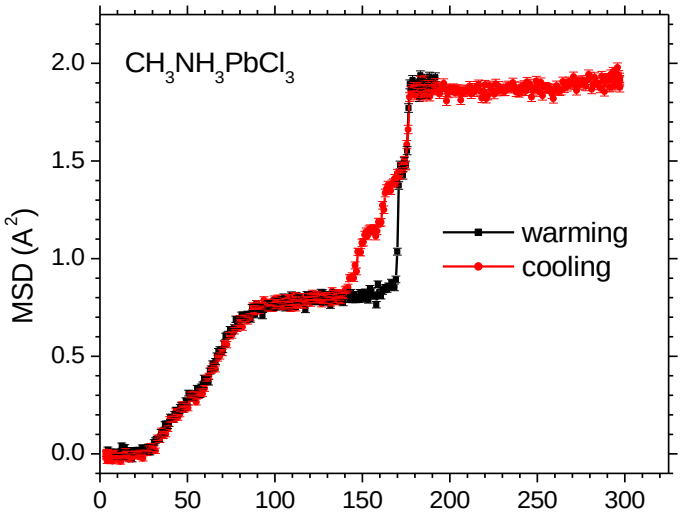
Dielectric constant and low T phase transitions: other halides

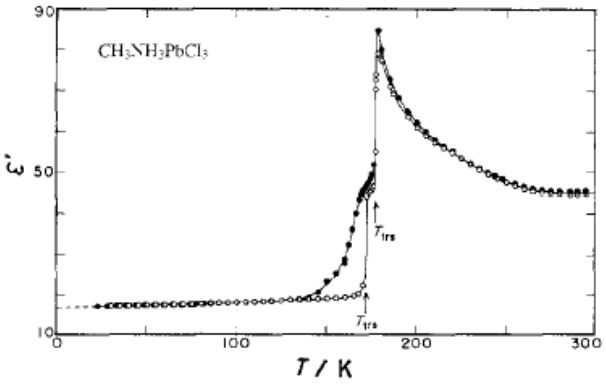
$CH_3NH_3PbBr_3$





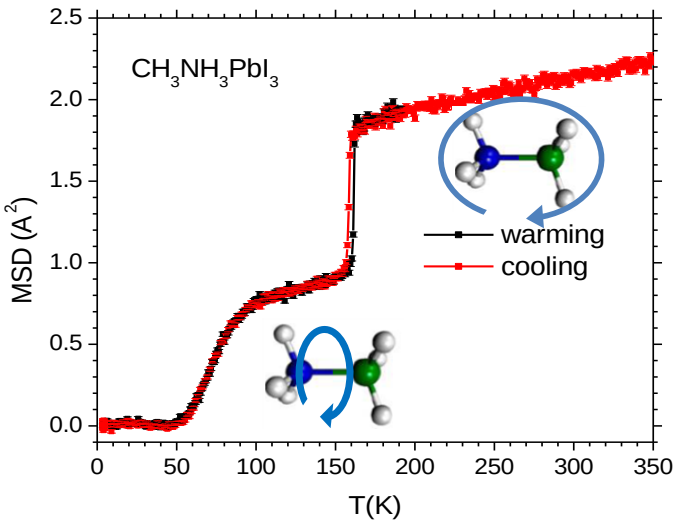
$CH_3NH_3PbCl_3$

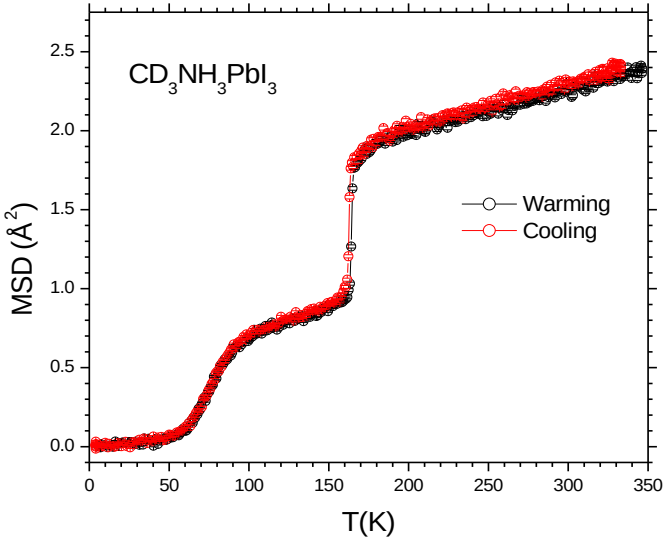




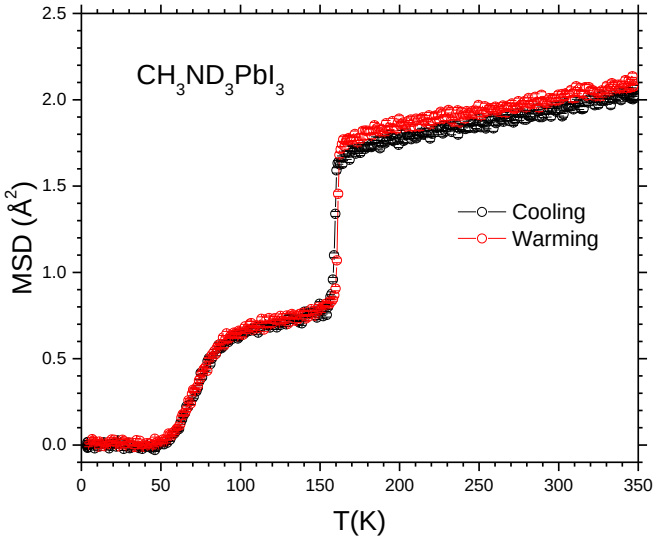
ε(1 kHz)

$MAPbI_3$: QENS and Partial Deuteration

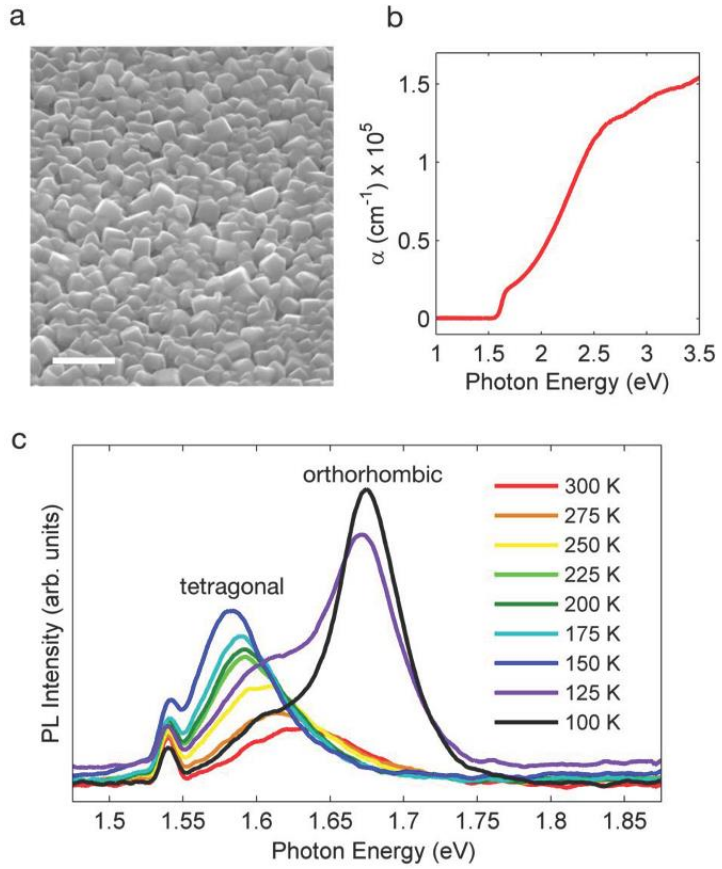




- MSD is characteristic of H atoms of MA cations: rotations around the C-N bond at low T and rotations of the bond at high T
- No significant isotope effect on phase transition or MSD values



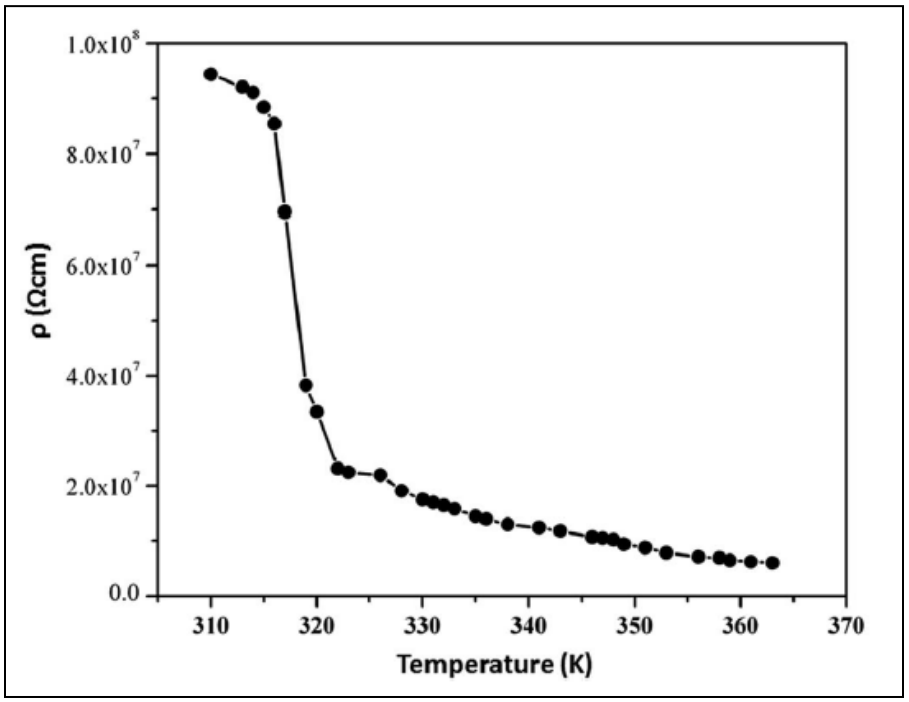
Structural transitions affect electronic properties



- Photoluminescence measured as a function of temperature
- PL is sensitive to electronic structure of PbI_3 sublattice
  - PbI_6 octahedra undergo additional tilts/distortions at the 160 K tetragonal → orthorhombic phase transition
  - Tilts change Pb-I-Pb bond angles, and this affects electronic structure
  - PL shifts to higher energy in orthorhombic phase

Sargent group, U. Toronto
B.R. Sutherland et al, Adv. Mater. 27, 53 (2015)

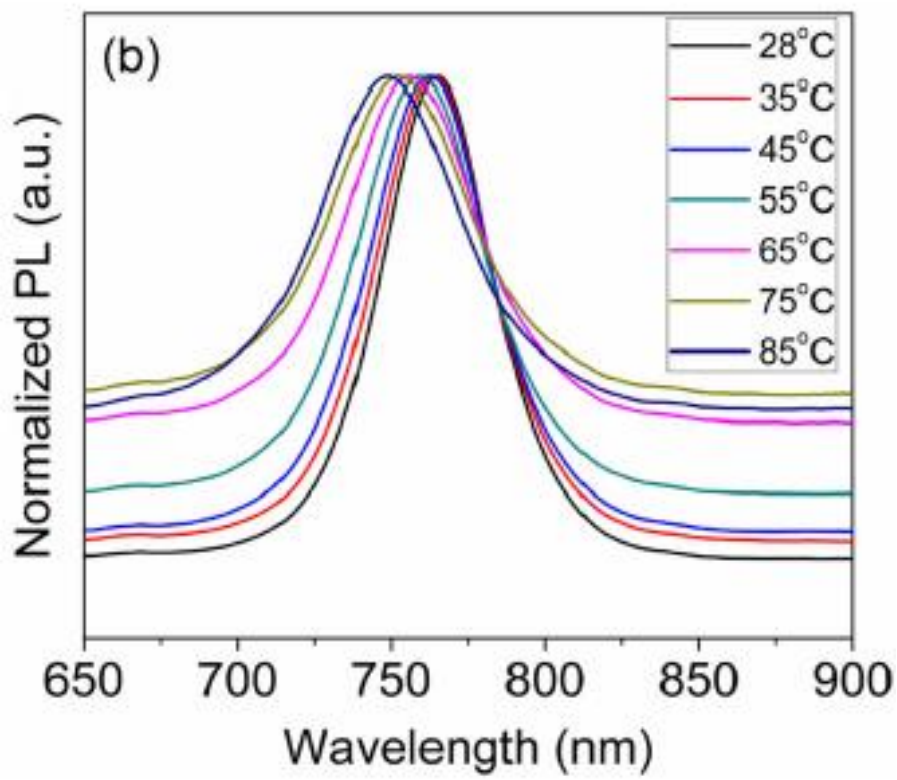
$MAPbI_3$: high temperature transition affects ionic conductivity



T. Baikie et al, J Mater Chem A (2015)

- Electrical conductivity vs temperature
  - Cubic → tetragonal phase transition occurs at 327 K
  - Conductivity is sensitive to Pb-I-Pb bond angles and lengths
- Activation energy for conduction in cubic phase is 0.38 eV
  - Consistent with ionic conductivity in other halides
  - Detailed understanding is still lacking

Does high temperature phase transition affect electronic properties?



- PL shifts with temperature
  - Associated with change of electronic band structure
  - Band gap should shift due to lattice expansion
  - Separating thermal effect from structural effect is difficult
- Short-range cubic structure could be tetragonal?
  - Single crystal diffraction shows R-point Bragg reflections in cubic phase, but broadened
  - Electronic structure would not change significantly across phase transition

Some remaining questions

- Lead-halogen phonons
  - Nature of phase transitions: displacive vs order-disorder
    - How do energies of PbI_6 rotational modes change with temperature? Are the modes overdamped?
  - Anharmonicity and ultralow thermal conductivity
  - What is magnitude of electron-phonon coupling?
  - Is tricritical nature of cubic-tetragonal transition important for PV properties?
- Electronic properties
  - Why are these materials so efficient for PV?
    - High dielectric constants? Defect and exciton screening?
    - Is Pb necessary for high efficiency?
  - Reason(s) for high carrier mobilities?
  - Can these materials be doped with electrons or holes?
  - Understand the effects of phase transitions on electronic properties?

Conclusions

- Hybrid perovskites are complex
  - Static and dynamic disorder due to organic cations
  - Structural phase transitions
  - Hydrogen bonds
- Structural complexity impacts properties important for photovoltaic applications
  - Dielectric constants
  - Optical properties
  - Thermal conductivity
  - Heat capacity
  - Thermal stability
- Neutron (and x-ray) scattering studies can provide a detailed microscopic understanding of the structures and dynamics of hybrid perovskites and other advanced materials

Thanks! Questions?

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